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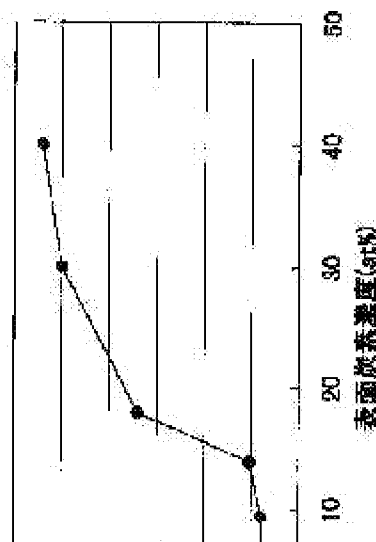
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## (54) TITANIUM HARDLY GENERATING COLOR CHANGE IN ATMOSPHERIC ENVIRONMENT AND MANUFACTURING METHOD THEREFOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a titanium hardly generating a color change in an atmospheric environment, and a manufacturing method therefor.  
SOLUTION: The titanium hardly generating a color change in an atmospheric environment is characterized by carbon of an average concentration of 14 atom % or less in a depth region between an extreme surface and 100 nm deep therefrom, and by having an oxide film of 12-40 nm thick on the extreme surface, on the titanium is characterized in that a ratio (X1/X2) of peak intensity X1



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## CLAIMS

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[Claim(s)]

[Claim 1]Titanium which does not produce discoloration easily in atmospheric environment which carbon concentration of an average in a 100-nm-deep range is less than 14at% from the outermost surface, and is characterized by having a 12-40-nm-thick oxide film in the outermost surface.

[Claim 2]In a surface X diffraction, a ratio ( $X1 / X2$ ) of the peak intensity (200)  $X1$  of TiC to the peak intensity (110)  $X2$  of titanium, Titanium which does not produce discoloration easily in atmospheric environment which is 0.18 or less and is characterized by having a 12-40-nm-thick oxide film in the outermost surface.

[Claim 3]Titanium which does not produce discoloration easily in the atmospheric environment according to claim 1 or 2 having an oxide film which produces an interference color on the surface.

[Claim 4]A manufacturing method of titanium which does not produce discoloration easily in the atmospheric environment according to claim 1 or 2 annealing after cold rolling and in a vacuum or inactive gas, and removing mechanically or chemically 1 micrometers or more of titanium surfaces after an appropriate time.

[Claim 5]A manufacturing method of titanium which does not produce discoloration easily in the atmospheric environment according to claim 1 or 2 removing mechanically or chemically 0.5 micrometers or more of the surface after cold rolling, and annealing in a vacuum or inactive gas after an appropriate time.

[Claim 6]pH performs electrolytic cleaning for 5 seconds or more in the range of current density  $0.05 - 5 \text{ A/cm}^2$  in an alkali solution of 11-15 after cold rolling, A manufacturing method of titanium which does not produce discoloration easily after an appropriate time in the atmospheric environment according to claim 1 or 2 annealing in a vacuum or inactive gas.

[Claim 7]A manufacturing method of titanium which does not produce discoloration easily in the atmospheric environment according to claim 3 carrying-out further characterized by processing which is anodized in an electrolytic solution or carries out heating oxidation in the atmosphere as post-processing of a manufacturing method given in any 1 paragraph of claims 4 thru/or 6.

[Claim 8]A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment of a statement in a manufacturing method given in any 1 paragraph of claims 4 thru/or 7 in any 1 paragraph of claims 1 thru/or 3 performing further steam treatment to which the surface is contacted for [ 10 seconds - ] 60 minutes at a 100-550 \*\* steam once or more.

[Claim 9]A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment of a statement in the manufacturing method according to claim 8 in any 1 paragraph of claims 1 thru/or 3, wherein said steam treatment is performed by a final process of a manufacturing process.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to titanium which does not produce discoloration easily in atmospheric environment, and a manufacturing method for the same, when used for outdoor type ways (a roof, a wall, etc.).

[0002]

[Description of the Prior Art]Since titanium shows the corrosion resistance which was extremely excellent in atmospheric environment, it is used for the roof of a seashore area, and a building-materials use like a wall. Since titanium begins to be used for roofing etc., about about ten years pass, but there is no example reported for corrosion to have occurred until now. However, there is a case dark in the titanium surface used over the long period of time depending on the operating environment where it discolors golden. Since discoloration is limited to a pole surface layer, it does not spoil the corrosion prevention function of titanium, but it may pose a problem from a viewpoint of design nature. In order to cancel discoloration, in carrying out wiping of the titanium surface using acid, such as \*\* fluoric acid, or removing a discoloring part by the light polish using abrasive paper and abrasive soap and processing a titanium surface [ large area / like a roof ], there is a problem from a viewpoint of workability.

[0003]Although not necessarily still solved fully about the cause which discoloration generates to titanium, when Fe and C which float in the atmosphere, SiO<sub>2</sub>, etc. adhere to a titanium surface and it generates, A possibility of generating when the thickness of titanium oxide of a titanium surface increases is suggested. As a method of reducing discoloration, it is reported to be effective to apply the titanium which has an oxide film of 100 Å or less in a titanium surface, and made surface carbon concentration less than 30at% so that it may be indicated by JP,2000-1729,A.

[0004]However, the surface analysis and the discoloration accelerated test of roofing made from titanium which produced discoloration in Japanese every place in order that artificers might prevent discoloration are used, The result of having considered carefully the influence of the thickness of an oxide film, and surface carbon concentration on discoloration, A means to solve radically the discoloration generated to the titanium which discoloration is not fully

prevented by JP,2000-1729,A but is used for it by the invention of a statement by atmospheric environment is in the state where it does not exist till the present.

[0005]

[Problem(s) to be Solved by the Invention]This invention provides titanium which prevents the discoloration generated when titanium is used in a roof and atmospheric environment like a wallplate in view of the above-mentioned actual condition, in which design nature does not deteriorate over a long period of time and which does not produce discoloration easily in atmospheric environment, and a manufacturing method for the same.

[0006]

[Means for Solving the Problem]Artificers use surface analysis and a discoloration accelerated test of roofing made from titanium which produced discoloration in Japanese every place, As a result of considering carefully influence of a titanium surface presentation exerted on discoloration, it found out that discoloration of titanium was promoted by existence of carbon concentration of a titanium surface or titanium carbide, titanium carbon nitride, and titanium nitride. Forming a comparatively thick oxide film in the surface found out acting effective in raising color fastness.

[0007]The place which this invention completes based on this knowledge, and is made into the gist is as follows.

(1) Titanium which does not produce discoloration easily in atmospheric environment which carbon concentration of an average in a 100-nm-deep range is less than 14at% from the outermost surface, and is characterized by having a 12-40-nm oxide film in the outermost surface.

(2) In a surface X diffraction, a ratio ( $X1 / X2$ ) of the peak intensity (200)  $X1$  of TiC to the peak intensity (110)  $X2$  of titanium, Titanium which does not produce discoloration easily in atmospheric environment which is 0.18 or less and is characterized by having a 12-40-nm oxide film in the outermost surface.

(3) Titanium which does not produce discoloration easily in atmospheric environment the above (1) having an oxide film which produces an interference color on the surface, or given in (2).

[0008](4) A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment the above (1) annealing after cold rolling and in a vacuum or inactive gas, and removing mechanically or chemically 1 micrometers or more of titanium surfaces after an appropriate time, or given in (2).

(5) A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment the above (1) removing mechanically or chemically 0.5 micrometers or more of the surface after cold rolling, and annealing in a vacuum or inactive gas after an appropriate time, or given in (2).

(6) pH performs electrolytic cleaning for 5 seconds or more in the range of current density 0.05 - 5 A/cm<sup>2</sup> in an alkali solution of 11-15 after cold rolling, A manufacturing method of titanium which does not produce discoloration easily after an appropriate time in atmospheric environment the above (1) annealing in a vacuum or inactive gas, or given in (2).

(7) A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment of a statement in the above (3) carrying-out further characterized by processing which is anodized in an electrolytic solution or carries out heating oxidation in the atmosphere as post-processing of a manufacturing method given in the above (4) thru/or any 1 paragraph of (6).

(8) In a manufacturing method given in the above (4) thru/or any 1 paragraph of (7), A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment of a statement in the above (1) performing further steam treatment which contacts the surface with a 100-550 \*\* steam for [ 10 seconds - ] 60 minutes once or more thru/or any 1 paragraph of (3).

(9) A manufacturing method of titanium which does not produce discoloration easily in atmospheric environment of a statement in a manufacturing method given in the above (8) in the above (1), wherein said steam treatment is performed by a final process of a manufacturing process thru/or any 1 paragraph of (3).

[0009]

[Embodiment of the Invention]Even if it tells atmospheric environment to a mouthful, it is possible that the environment completely changes with an industrial area, pastoral land, and areas from the seashore, and the environmental factors exerted on discoloration of titanium differ. Also in the same area, there are titanium which produces discoloration, and titanium which is hard to produce, and a possibility of having received the influence by the constituent element in titanium or the difference in a production history can be considered.

[0010]This invention persons carry out the exposure examination of the titanium which sorted out the area where environment differs in Japanese every place, and performed various kinds of surface finish in order to clarify such environmental influence and the construction material factor which are exerted on discoloration of titanium, and. The roof made from titanium which actually produced discoloration was removed, and the titanium surface was analyzed.

[0011]As a result of continuing such examination, as shown in drawing 1, discoloration of titanium found out that it was easy to produce the thing which has the high carbon concentration of a titanium surface. Drawing 1 shows a relation with the average carbon content of the range of 100 nm from the measurement result of the color difference before and behind the examination of the titanium plate which carried out the exposure examination for four years in Okinawa, and the titanium surface measured using the Auger-analysis machine. As an environmental factor which promotes discoloration, the influence of acid rain clarified the large thing.

[0012]This invention prescribes the carbon concentration of a titanium surface, as shown above (1), but. When titanium is used in atmospheric environment, the rate of dissolution of titanium is made to increase, as a result, the thickness of titanium oxide of a titanium surface increases, and the carbon which exists in a titanium surface produces an interference color, and depends it on it being thought that coloring is generated. About a carbon content, since generating of discoloration of the carbon content in the range of 100 nm in the field below 14at% is controlled from the outermost surface as shown in drawing 1, it is necessary to make

carbon concentration into less than [ 14at% ].

[0013]The solid-solution limit of carbon in titanium is about 1 at% at 700 \*\*, and unless titanium is dissolved in application of pressure, carbon of the quantity which promotes discoloration does not invade into titanium. Rolling oil decomposes, for example during cold-rolling, that carbon invades into titanium trespasses upon a titanium surface, and the case where carbon invades is applied to the surface layer of titanium with the case where annealing or vacuum annealing is carried out further, ion sputtering, an accelerator, vacuum evaporation or an electric discharge machine, etc. If the carbonaceous invasion to a titanium surface is extremely limited to a surface layer in these cases, there will be no influence of [ to the extent that discoloration is promoted ]. That is, it does not become a big problem, in order to form titanium oxide and for interferential action not to color, even if the rate of dissolution of titanium of these surface layers increases if the penetration depth to a carbonaceous titanium surface is limited to a pole surface layer (for example, less than 10 nm).

[0014]however, concentration of carbon in a titanium surface -- when a layer exceeds several 10 nm, coloring will be produced by interferential action. In this invention, since a very good relation is obtained between the average carbon concentration of 100 nm, and discoloration from the surface, color fastness can be raised by leaps and bounds by making carbon concentration of the average in the range of 100 nm less than 14at% from the surface. In addition, color fastness can be further raised by leaps and bounds by making a comparatively thick oxide film form in the outermost surface.

[0015]Not less than at least 12 nm of thickness of the oxide film which has such the characteristic is needed. Protection feature sufficient in less than 12 nm cannot be exhibited. However, when oxide film thickness exceeds 40 nm, in order for the stress which acts on an oxide film to increase, for a crack to occur selectively and for a protection feature to fall, the oxide film thickness needs to be 40 nm or less. The range of the most desirable oxide film thickness is 20-30 nm.

[0016]The existence of the carbonaceous invasion to such a titanium surface can be measured using an Auger-analysis device. That is, from a titanium surface, Auger analysis can be conducted at intervals of 5 nm or 10 nm, and it can measure to a depth of not less than at least 100 nm, and can be considered as average carbon concentration using those average value.

[0017]Although discoloration of titanium is promoted by existence of carbon, discoloration of titanium is promoted, when carbon combines with titanium and forms titanium carbide. In many cases, such titanium carbide is TiC, but although it is quantitatively less than TiC, what contains the thing and nitrogen with high titanium concentration in carbide like  $Ti_2C$  or  $Ti(C_xN_{1-x})$  exists. However, TiC(s) are quantitative most carbide and the abundance of other titanium carbide and titanium carbon nitride can also be reduced by reducing the abundance of TiC. In order to grasp this quantitatively, it is made for the ratio ( $X1 / X2$ ) of the peak intensity (200) X1 of TiC to the peak intensity (110) X2 of titanium to become 0.18 or less in a surface X diffraction so that it may specify above (2).

[0018]The information from a titanium surface drawing 2 using the thin film X-ray diffractometer obtained (200) X ray peak intensity (X1) of TiC of a titanium surface, It asks for the relation

between a ratio ( $X1 / X2$ ) with the peak intensity (110) ( $X2$ ) of titanium metal, and the color difference before and behind the examination in the discoloration accelerated test in a laboratory. When the abundance ratio of TiC exceeds 0.18, the value of color difference increases, namely, it turns out that discoloration is promoted.

[0019]Thin film X diffraction measurement was performed using RINT1500 by Rigaku Corp. The bulb measured on the conditions whose incidence angles [ as opposed to / in 50 kV and tube current / tube voltage / (/ using 150 mA) and a thin film attachment / a specimen surface at the product made from Cu ] are 0.5 degree. 0.40 mm, 8.00 mm, and 5.00 mm were used for the divergent slit, scattering slit, and light-receiving slit of a wide angle goniometer, respectively. Using the monochromator, the light-receiving slit of the monochromator was 0.60 mm. The field internal version of the specimen was carried out with the revolving speed of 40 revolutions per minute, and the scan speed measured twice on the conditions which are a part for /. As mentioned above, it becomes possible by reducing the precipitation amount of the titanium carbide in a titanium surface to raise the color fastness of titanium substantially.

[0020]Identification of the titanium carbide in a titanium surface can be performed also by carrying out transmission electron microscopic observation of the test piece surface from a cross sectioned direction. However, since an observation area is restricted to a part, it is not necessarily easy to clarify the existence of generating of discoloration, the precipitation amount of titanium carbide, and a fixed-quantity relation with size in this case. Therefore, in this invention, the technique of measuring the surface layer of a comparatively large area like thin film X-rays measurement is adopted. However, when the equivalent area of a titanium surface is observed using a transmission electron microscope and a deposit of titanium carbide is not observed at all, the color fastness outstanding, of course is shown.

[0021]As a gestalt with which titanium is used into atmospheric environment, there are many cases of a titanium plate or a belt. In the above (4), the manufacturing method which is hard to discolor about the titanium which takes such a gestalt is indicated. Usually, as for the titanium plate and belt which are used for an outdoor type way, elasticity-ization of a raw material is attained so that cold-rolling may be carried out even to predetermined thickness by cold rolling, annealing may be received from 650 \*\* after that in the temperature region near 850 \*\* and various kinds of processings can be performed. It may originate in the survival to the titanium surface of cold rolling oil, carbon may trespass upon a titanium surface, and the titanium plate and belt which are manufactured through such a manufacturing process may promote discoloration of a titanium plate.

[0022]In such a case, the color fastness of titanium can be substantially improved by removing mechanically or chemically the field where the field and the titanium carbide, titanium carbon nitride, and titanium nitride in which carbon near the titanium surface condensed deposit. Mechanical removal can be attained by immersing titanium into the acidic solution which can adopt the method of making a surface layer exfoliating using polish or a blast and in which titanium is eluted about a chemical removal method, or an alkali solution. however, adopt a mechanical or chemical removal method -- a 1-micrometer order becomes indispensable [ that the field upon which carbon has trespassed removes 1 micrometers or more-deep titanium for



a certain reason (it depends for the penetration depth of carbon to a titanium surface on heat treatment temperature and time) ]. As the method of dissolving titanium efficiently, the technique of immersing titanium into the mixed acid solution of nitric acid and fluoric acid is especially preferred.

[0023]In the process of manufacturing cold-rolling, annealing board, and belt of titanium which are hard to discolor, After cold rolling, carrying out annealing carried out for elasticity-izing of a raw material in the environment which enclosed the inside of a vacuum or inactive gas can reduce oxidation of titanium, it can skip a subsequent pickling process etc., and is a desirable manufacturing method from a viewpoint of productivity. however, concentration of the carbon formed in the titanium surface of the cold rolling process -- a field and titanium carbide. In not removing the deposit field of titanium carbon nitride and titanium nitride using a mechanical or chemical technique, The field where the field where carbon concentration is high, and the above-mentioned compound deposited is formed in the surface of the last titanium cold-rolled board or a belt, and discoloration of titanium may be promoted when these titanium plates or belts are used into atmospheric environment.

[0024]In such a case, can adopt as the above (5) like a statement the method of making a surface layer exfoliating using mechanical polish or a blast etc. after cold rolling, and about a chemical removal method. It can attain by immersing titanium into the acidic solution in which titanium is eluted, or an alkali solution. Although it is a penetration depth of carbon in the titanium surface at the time of cold rolling, Since there is no invasion by diffusion of carbon at the time of annealing as compared with the case where it removes after annealing shown above (4), A penetration depth is about 0.5 micrometer and can improve remarkably the color fastness of the titanium plate annealed in a vacuum or inactive gas, or a belt by removing mechanically or chemically the titanium surface of the range of at least 0.5 micrometers or more.

[0025]The above (6) is concerned above (5) and aimed at raising productivity substantially about the cold-rolled titanium plate or belt by performing improvement in degreasing and color fastness simultaneously at one process. Degreasing is performed in many cases by usually carrying out the spray of immersion or the alkali solution into an alkali solution. However, in order to aim at improvement in discoloration-proof and to dissolve a titanium surface, it is not enough just to carry out the spray of immersion or the alkali solution into an alkali solution.

[0026]As shown above (6), when pH carries out electrolytic cleaning into 15 or less alkali solution or more from 11, degreasing and the titanium surface which are made into the purpose can be dissolved. Since  $\text{TiO}_2$  which exists in a titanium surface exists stably when pH is less than 11, a titanium surface cannot be dissolved efficiently. When pH is 15 or more, titanium can be made eluted efficiently, but using the solution of a strong base makes pH 15 a maximum, in order for titanium itself to dissolve at a remarkable speed that it is not desirable on operation, and only by being immersed in a solution.

[0027]As for polarity, since as for an electrolytic condition the lytic reaction of titanium is promoted when titanium serves as the (-) pole, removal for organicity is performed effectively and titanium serves as the (+) pole, it is preferred to change from (+) to (-) or (+) from (-).

About current density, if there is no current density more than  $0.05 \text{ A/cm}^2$  at least, the removal for adhering organicity and lytic reaction of titanium cannot be produced. About electrolysis time, 5 seconds or more are needed at least. If current density is made high, since quantity of electricity needed is generally arranged in current density x time, business time will decrease, but. Since in the case of the above electrolytic cleaning the current of a remarkable rate is consumed by oxygen evolution in the anode and consumed by hydrogen generating by the negative pole, also when current density is made high, as electrolysis time, 5 seconds or more are needed at least. About current density, if  $5 \text{ A/cm}^2$  is exceeded, since generation of heat of a solution will become remarkable and will pose an operation top problem, let  $5 \text{ A/cm}^2$  be a maximum of electrolytic current density.

[0028]Titanium can manufacture various kinds of coloring material using the interference color to which the thickness of the titanium oxide of a titanium surface was changed. Since design nature can be given with the corrosion resistance which was excellent in titanium, such a coloring titanium material is used as the wall panel for which design nature is needed with corrosion resistance, or a raw material for roofs. A coloring titanium material is manufactured by methods, such as air oxidation or anodization in solution. The above (3) of this invention and the above (7) which is the manufacturing method are related with the coloring titanium material manufactured by the anodization in an oxidation style or an alkaline aqueous solution, and an acidic solution.

[0029]Since the titanium oxide layer is formed in the titanium surface, a coloring titanium material is considered to excel about the color fastness at the time of being used in atmospheric environment as compared with pure titanium. However, depending on an operating environment, the coloring titanium material considered to excel in such color fastness may also produce discoloration. concentration of the carbon which exists in the ground of a titanium oxide layer like the case of pure titanium as for discoloration of coloring titanium -- it is promoted by deposit of a field or titanium carbide, titanium carbon nitride, and titanium nitride. therefore, concentration of the carbon which exists in the lower part of a titanium oxide layer also from a viewpoint which prevents discoloration of coloring titanium -- it becomes important to remove a field or the deposit field of titanium carbide.

[0030]In order to usually make it color using interferential action, as the thickness of an oxide film is in the range of several 10 to several 100 nm and it mentioned above in the coloring titanium material, as compared with the invasion distance (micrometer of order) of carbon of a titanium surface, it is small. Therefore, in carbon's having condensed, or titanium carbide, titanium carbon nitride, and titanium nitride making the titanium which deposited on the surface the charge of a start material and manufacturing a coloring titanium material. the ground (titanium metal side) of a titanium oxide layer -- carbonaceous concentration -- since a field or the deposit field of titanium carbide remains, the color fastness of a coloring titanium material is reduced. therefore, concentration of the carbon which exists in the ground portion of titanium oxide -- the color fastness of a coloring titanium material can be raised by removing a field or titanium carbide, titanium carbon nitride, and titanium nitride. That is, coloring titanium

excellent in color fastness can be obtained by immersing this into an electrolytic solution, and carrying out anode electrolysis by making into the charge of a start material the titanium manufactured based on titanium or the manufacturing method shown by (6) from the above (4), or heating in the atmosphere.

[0031]Color fastness can be further raised by carrying out steam treatment of the titanium manufactured according to (7) from the above (4) once [ at least ] or more further. Although not enough solved about the mechanism of the improvement in color fastness by steam treatment, it is presumed that the defective part of the passive film of a titanium surface is restored. It is thought that the water molecule is participating in the restoration closely. Therefore, as a temperature of steam treatment, the temperature of not less than at least 100 °C is needed. In less than 100 °C, sufficient thermal energy required for restoration of the defective part of passive film cannot be obtained. However, if steam temperature exceeds 550 °C, since the oxide film of a titanium surface grows thickly, and turns into a porosity coat and a protective action falls, it is not desirable.

[0032]By spraying the steam which was considered that a reaction advances quite quickly in the above-mentioned temperature requirement about processing time, and held the titanium material in a 10-second or more steam, or was made into the above-mentioned temperature on a titanium material, a steam can be made to be able to contact and color fastness can be raised substantially. However, in order to obtain the result of having been stabilized, holding or spraying for several minutes is preferred. Although color fastness does not deteriorate at all by the steam treatment exceeding 60 minutes, since the effect of improvement in color fastness was saturated mostly, 60 minutes was made into the maximum.

[0033]Although pretreatment which hits carrying out steam treatment is not especially specified, when organic dirt remains in the titanium surface, in order for the effect by steam treatment to decrease, it is necessary to process a titanium surface using a suitable solvent or the degreaser of weak alkali. However, such pretreatment is not special at all and is performed by the usual degreasing process. Tap water etc. can be used also about the water used for steam treatment. However, since it thinks also when it has an adverse effect on a test result depending on the difference in the component of water, it does a preliminary test etc., in using fresh water etc. as it is, and it is considered [ be / using tap water / it / better ] when a good test result is not obtained.

[0034]

[Example]Table 1 the titanium in which the carbon concentration of the average in the range of 100 nm differs from the outermost surface, The color difference of titanium before and behind an examination when the pH of a solution carries out an immersion test for two weeks in 60 °C in the sulfuric acid solution of three (influence of acid rain) is measured, and the result of having considered the influence of carbon concentration on discoloration is shown. Brightness  $L^*$  and chromaticity  $a^*$  which are asked for measurement of color difference based on JIS Z

8730,  $b^*$  -- it asked according to color difference  $\Delta E_{ab}^*$  [from difference  $\Delta L^*$  before and behind each measurement,  $\Delta a^*$ , and  $\Delta b^*$  ]  $^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ .

[0035]As shown in Table 1, these titanium materials contain cold-rolled material with the flat surface, the abrasive which raised relative roughness, etc., but. Also in the titanium material of which surface finish, by making carbon concentration of an average in the surface less than 14at% in accordance with this invention method, and making oxide film thickness in the outermost surface into the range of 12-40 nm shows that the color difference before and behind an examination shows about 5 or less and the outstanding color fastness.

[0036]Surface carbon concentration measurement is measured using an Auger-analysis machine.

In this measurement, a result containing dissolution carbon and carbon in titanium carbide is brought, and dissolution carbon and the carbon contained in carbide cannot be separated. That is, a result containing the carbon contained in dissolution carbon and carbide is brought to the carbon concentration of the titanium surface shown in Table 1.

[0037]Table 2 shows the result of having investigated the influence of TiC which is the same method as \*\*\*\* and it has on discoloration of titanium about the titanium in which the surface amounts of TiC(s) differ, using thin film X-ray diffractometer. As shown in Table 2, the integrated intensity of the signal considered that the abundance of TiC originates in TiC in thin film X diffraction measurement was used. However, if it originates in TiC, the peaks of idea \*\*\*\* X-rays differ a pure peak position and a little in thin film X-rays measurement.

As for the compound described to be TiC in this invention, possibilities that the grating constant changed are idea \*\*\*\* by dissolving nitrogen a little in a compound.

As for this invention steel whose signal strength resulting from TiC is the zero below a detection limit, it turns out that color difference shows the color fastness which was extremely excellent with about about five.

[0038]Table 3 anneals the titanium belt cold-rolled to a thickness of 0.6 mm in argon gas, The measurement result of the color difference before and behind an examination when a discoloration accelerated test is carried out after an appropriate time in the sulfuric acid solution of pH 3 for the material removed in the depth which displayed the surface layer for this titanium belt with the chemical-lysis method and the mechanical removal method is shown. As shown in Table 3, as compared with the titanium material which has not removed the titanium belt from which the several micrometers surface layer was removed by the chemical and mechanical method, it turns out that the value of color difference shows about 5 or less and the extremely outstanding color fastness.

[0039]Table 4 shows the measurement result of the color difference before and behind an examination when pH immerses the titanium belt which dissolved the several micrometers titanium surface or from which the several micrometers surface layer was removed by mechanical polishing in the sulfuric acid solution of three by immersing the titanium belt with which thickness was cold-rolled to 0.4 mm into a nitric-hydrofluoric acid solution. As shown in Table 4, it turns out that such a titanium belt shows the extremely outstanding color fastness.

[0040]pH the titanium belt with which cold-rolling of Table 5 was carried out to a thickness of 0.5 mm in the alkali solution of 9 to 15, Electrolytic cleaning is carried out on various kinds of current density conditions, and after performing annealing of 8 hours at 640 \*\* in argon gas

and a vacuum after an appropriate time, the result of having measured the color difference before and behind an examination when the immersion test for 14 days was carried out in the sulfuric acid solution whose pH is 60 \*\* of 3 is shown. As shown in Table 5, when pH carries out electrolytic cleaning in the solution of 11 to 15 in accordance with this invention method, it turns out that the outstanding color fastness is shown.

[0041] Table 6 shows the result of having measured the carbon concentration of the average of the range of 100 nm using the Auger-analysis method from the outermost surface before processing of the coloring titanium manufactured by the anode oxidation method in the inside of 1% of phosphoric acid solution and air heating, and the result of having evaluated the color fastness of the coloring titanium material (as blue as gold). As shown in Table 6, it turns out that the coloring titanium manufactured considering the titanium which made average carbon concentration less than 10at% in accordance with this invention method as a raw material shows the outstanding color fastness in the discoloration accelerated test which used pH 3 sulfuric acid solution. In Tables 3-6, what performed steam treatment shows the color fastness further outstanding compared with what is not being processed.

[0042]

[Table 1]

	チタン表面*の平均炭素濃度	最表面の酸化膜厚み	色差(変色試験前後)
本発明 1	3 . 5 (at%)	1 2 (nm)	4
本発明 2	5 . 5	2 0	4 . 5
本発明 3	7 . 5	3 7	4 . 8
本発明 4	9	2 2	5
本発明 5	1 3	1 3	4 . 9
比較例 1	1 5	6	1 3
比較例 2	2 4	5	2 2
比較例 3	3 0	7	2 5
比較例 4	3 7	9	2 7
比較例 5	7 . 5	5	1 5 . 8

\* 最表面から 1 0 0 n m

[0043]

[Table 2]

	ピーク強度比 ( $x_1 / x_2$ )	最表面の酸化膜厚み	色差(変色試験前後)
本発明 1	0	1 2	3 . 4
本発明 2	0 . 1	2 0	4 . 2
本発明 3	0 . 1 6	3 7	4 . 3
比較例 1	0 . 1 4	5	1 1
比較例 2	0 . 2	6	1 2
比較例 3	0 . 2 2	4	2 0
比較例 4	0 . 2 4	3	2 2
比較例 5	0 . 2 6	5	2 8

[0044]

[Table 3]

	板厚 (mm)	除 去 方 法	除去深さ ( $\mu\text{m}$ )	水蒸気処理の 有無及び条件	色差
本発明 1	0.5	研磨	1.5	無し	5.0
本発明 2	0.6	50℃の硝酸+フッ酸溶液中で1分間浸漬	5.0	無し	4.6
本発明 3	0.4	50℃の硝酸+フッ酸溶液中で1分30秒間浸漬	7.0	無し	4.9
本発明 4	0.4	50℃の硝酸+フッ酸溶液中で1分30秒間浸漬	—	有り(120℃で10分間)	1.8
比較例 1	0.7	研磨	0.1	無し	18.5
比較例 2	0.5	50℃の硝酸+フッ酸溶液中で10秒間浸漬	0.2	無し	15.8

[0045]

[Table 4]

	板厚 (mm)	除 去 方 法	除去深さ ( $\mu\text{m}$ )	水蒸気処理の 有無及び条件	色差
本発明 1	0.6	研磨	0.7	無し	4.5
本発明 2	0.5	50℃の硝酸+フッ酸溶液中で30秒間浸漬	2.0	無し	3.9
本発明 3	0.6	研磨	0.7	有り(350℃で2分間)	1.6
比較例 1	0.4	研磨	0.2	無し	15.8
比較例 2	0.6	50℃の硝酸+フッ酸溶液中で15秒間浸漬	0.3	無し	16.9

[0046]

[Table 5]

	板厚 (mm)	溶液組成と液のpH	電 解 条 件	水蒸気処理の 有無及び条件	色差
本発明 1	0.5	pHが11のNaOH水溶液	極性(-)→(+)で $2\text{A}/\text{cm}^2$ の10秒ずつ電解	無し	4.6
本発明 2	0.6	pHが12のNaOH水溶液	極性(-)→(+)で $5\text{A}/\text{cm}^2$ の5秒ずつ電解	無し	4.6
本発明 3	0.7	pHが14のNaOH水溶液	極性(-)→(+)で $0.05\text{A}/\text{cm}^2$ の5秒ずつ電解	無し	4.7
本発明 4	0.4	pHが15のNaOH水溶液	極性(+)→(-)で $5\text{A}/\text{cm}^2$ の5秒ずつ電解	無し	5.3
本発明 5	0.5	pHが11のNaOH水溶液	極性(-)→(+)で $2\text{A}/\text{cm}^2$ の10秒ずつ電解	有り(120℃で10秒間)	2.1
比較例 1	0.6	pHが9のNaOH水溶液	極性(-)→(+)で $5\text{A}/\text{cm}^2$ の5秒ずつ電解	無し	22.5
比較例 2	0.5	pHが10のNaOH水溶液	極性(-)→(+)で $2\text{A}/\text{cm}^2$ の10秒ずつ電解	無し	19.8

[0047]

[Table 6]

	板厚 (mm)	処理前の炭素 濃度 (at%)	発 色 方 法	水蒸気処理の 有無及び条件	色	色差
本発明 1	0.6	7.5	1%リン酸溶液中での陽極酸化法	無し	金色	4.6
本発明 2	0.5	5.5	1%リン酸溶液中での陽極酸化法	無し	青色	3.5
本発明 3	0.7	6.2	大気加熱法	無し	金色	5.2
本発明 4	0.4	8.0	大気加熱法	無し	青色	3.2
本発明 5	0.5	5.5	1%リン酸溶液中での陽極酸化法	有り(450℃で2分間)	青色	1.6
本発明 6	0.7	6.2	大気加熱法	有り(120℃で10分間)	金色	1.8
比較例 1	0.7	23.5	1%リン酸溶液中での陽極酸化法	無し	金色	28.5
比較例 2	0.6	32.5	大気加熱法	無し	青色	17.5

[0048]

[Effect of the Invention]following this invention, as shown above -- carbon in a titanium surface -- the titanium which controlled the deposit of concentration or titanium carbide, titanium

carbon nitride, and titanium nitride has the extremely outstanding color fastness.  
It is effective in especially the use in outdoor environment like a roof or a wall panel.

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[Translation done.]